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13. ABSTRACT (Maximum 200 words) There were two objectives for this research. One was to study the water resistance of various modified soy protein adhesives on fiberboard as packaging box. The other was to investigate the effect of drying temperature on the adhesive performance of the soy protein. In the studies, the soy protein isolate (SPI) was modified using sodium dodecyl sulfate (SDS) and guanidine hydrochloride (GuHCl). Adhesion performance of the modified SPI on fiberboard was studied. Water resistance of the modified SPI adhesives was examined following modified ASTM D5570-94. The SDS-modified SPI containing 90% protein met the requirement: the percentage of water-soluble-mass of adhesive should be less than 2%. The wet shear strength test showed 100% cohesive failure within fiberboard. This indicates the modified SPI has good water resistance. The effect of drying temperature on adhesive performance of the SDS-modified SPI on fiberboard was then investigated. The drying temperature was found to affect the final adhesion strength significantly. The wet shear strength tests showed that the controlled specimens prepared at low pressure exhibited almost no cohesive failure within fiberboard while heat-treated (50 – 90°C) specimens exhibited completely cohesive failure within fiberboard. This information will be useful reference for low cost adhesive processing in the future.			
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Enclosure 1

Adhesion Performance of Modified Soy Protein Adhesive

(G# DAAD19-01-1-0570)

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Statement of the problem studied

Phenol and urea formaldehyde-based and/or thermoplastic resin-based adhesives are commonly used in the Army system for applications of plywood, particleboard, packaging, labeling applications, etc. These adhesives have caused unpleasant environmental problems in processing, distribution, application, and waste management. Also, they are harmful to human being. However, soy-based adhesives are produced from renewable agricultural resources and are environmentally friendly, and hence they are getting more and more attention.

Usually, soy protein adhesives have low gluing strength and water resistance. These limit the wide utilization of soy protein adhesives. In our previous research, modification of soy protein has showed improvement in shear strength. One of water resistance specifications of adhesives for fiberboard packaging application is the mass solublized in water should be less than 2% by ASTM D5570-94 standard. The objective of this research was to study the water resistance of various modified soy protein adhesives on fiberboard as packaging box following

ASTM D5570-94. The shear strength and failure mode when the specimen was still wet (the wet shear strength) were also examined to further evaluate the water resistance.

One of the procedures of preparing the soy protein and the adhesive is drying. Therefore, the second objective of this research was to investigate the effect of drying temperature on the adhesive performance of the soy protein.

Summary of the most important results

Guanidine hydrochloride (GuHCl) modified soy protein isolate (SPI) adhesive had much higher percentage of water-soluble-mass than that of unmodified adhesives (Tables 1 and 2) because of high concentration of GuHCl in the adhesive. The water-soluble-mass of sodium dodecyl sulfate (SDS) modified SPI, containing 82% protein, was 6.5% (Table 1), which was higher than the ASTM D5570-94 requirement (2%). Therefore, SPI containing higher protein (90%) was used, and several SDS concentrations were studied. The 1% SDS-modified SPI containing 90% protein was found to have 1.75% water-soluble-mass (Table 2), which met the ASTM D5570-94 requirement, and to exhibit 100% cohesive failure within fiberboard for the wet strength test (Table 4).

Drying had significantly effect on the adhesion performance of SPI adhesives (Tables 5 and 6). Heat-treatment (50 – 90°C) could further improve adhesive strength and water resistance. The percentage of cohesive failure within fiberboard for the wet strength test also increased for the heat-treated adhesives. The SDS-modified SPI with 82% protein treated at 50 – 90°C showed 100% cohesive failure within fiberboard (Table 5).

This study showed that the modified SPI with either 90% or 82% protein can be a good adhesive for the fiberboard but can be selected based on total processing cost and further specification testing.

Listing of publications and technical reports

1. Zhikai Zhong, Donghai Wang, X. Susan Sun, and J. A. Ratto. Water Resistance of modified Soy Protein Adhesives and the Effect of Drying Temperature. *Manuscript in preparing*.

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Appendixes

I. Sample preparation.

To prepare control or modified SPI adhesives, 12 grams of SPI were dissolved in 100 grams of aqueous solution without or with the modifier (3% SDS or 1M GuHCl), and stirred for 2 h. Modifiers and their concentrations that gave the highest adhesion performance for fiberboard (10-13) were used in this experiment except the high-protein-content SPI (90%), for which several SDS concentrations were used.

To study the effect of drying on adhesive performance, the 3% SDS-modified SPI adhesive slurry was poured into a tray, and was dried in air-oven at various temperatures (30, 50, 70, and 90°C). The dried samples were film-like, and were powdered using a Cyclone Sample Mill (UDY Corporation, Fort Collins, CO). To prepare the drying-treated SDS-modified adhesive, about 15 grams of oven-dried powder were dissolved in 100 grams of distilled water, and stirred for 2 h. The amount of the oven-dried powder, which was used to prepare the drying-treated SDS-modified adhesive, was calculated according to its water content, and made sure that the adhesive had same SPI and SDS contents as the control.

For water-soluble-mass measurement, the adhesive slurry was brushed onto a piece of solid fiberboard V2S (6" × 3.5") until the entire area was completely wet (about 1.5 ± 0.1 mg/cm² protein solid concentration). The amount of slurry on each fiberboard was controlled by using a consistent brushing procedure to minimize variations. The applied area was 6" × 3.5". The slurry-brushed fiberboard was allowed to rest at room temperature for 10 min, and then was

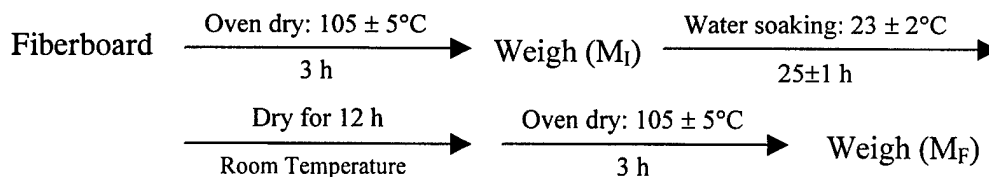
placed onto a larger piece of aluminum foil (7" × 5.5"). Made sure the foil facing to the slurry-brushed side. The aluminum foil was sprayed a layer of mould-releaser before assembling. After that, the assembly was pressed at 100°C, 2 MPa for 5 min using a Hot Press (Model 3890 Auto "M", Carver Inc., Wabash, IN), and then the aluminum foil was removed from the fiberboard.

The fiberboard specimens for shear strength testing were prepared according to the modified TAPPI UM633 method. The adhesive slurry was brushed onto one end of both two pieces of fiberboard (6" × 3.5") until the entire area was completely wet (about 1.5 ± 0.1 mg/cm² protein solid concentration). The amount of slurry on each fiberboard was controlled by using a consistent brushing procedure to minimize variations. The applied area on each end was 6" × 1". The two pieces of slurry-brushed fiberboard were allowed to rest at room temperature for 10 min, and then were pressed together at 100°C, 2 MPa for 5 min using the Hot Press.

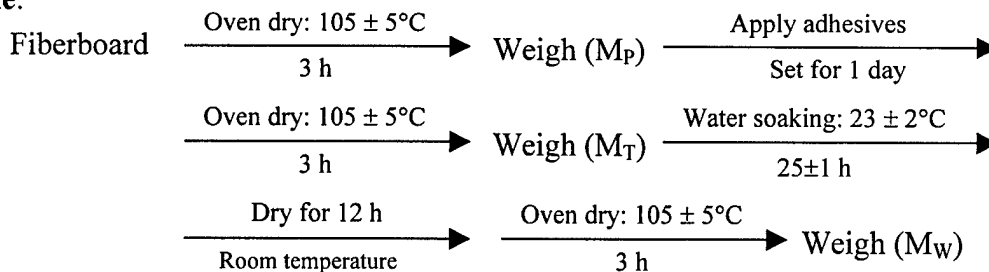
II. Measurement of the percentage of water-soluble-mass.

The following are the procedure to measure the percentage of water-soluble-mass (according to the modified ASTM D5570-94):

Reference:



Sample:



Water-soluble mass (M_R) in **Reference** was: $M_R = M_I - M_F$

The value presented is the mean of three replicas.

The mass of adhesive (M_A), which was applied onto **Sample**, was calculated by:

$$M_A = M_T - M_P$$

The percentage of water-soluble-mass of adhesive in **Sample** was:

$$S_A \% = \frac{M_T - M_W - M_R}{M_A} \times 100$$

The value presented is the mean of three replicas.

III. Shear strength tests.

The fiberboard assemblies prepared for shear strength testing were preconditioned at 23°C and 50% RH for 48 h and then were cut into five 25 mm-wide specimens. These were preconditioned further for 5 days in a conditioning room (23°C, 50% RH). An Instron universal testing machine (Model 4465, Canton, MA) with a crosshead speed of 25.4 mm/min was used. The shear strength at maximum load was recorded, and each value presented is the mean of 5-8 specimens. Failure mode of test specimen was also determined by naked eyes observation.

For shear strength of soaked sample, 5-8 of the 25 mm-wide specimens for each set of conditions were soaked in tap water at 23°C for 24 h. Then they were dried at 23°C and 50% RH for 5 days, and shear strength was tested as described above.

For wet shear strength, 5-8 of the 25 mm-wide specimens for each set of conditions were soaked in tap water at 23°C for 24 h. Then they were taken out of water and tested as described above immediately.

IV. Results and tables.

Table 1. Water-soluble-mass of various SPI (82% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 2 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Water-soluble-mass, S_A (%)
SPI	5.62 ± 4.62
3% SDS-modified SPI	6.52 ± 0.63
1M GuHCl-modified SPI	43.93 ± 1.96

Table 2. Water-soluble-mass of various SPI (90% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 2 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Water-soluble-mass, S_A (%)
SPI	5.96 ± 4.97
1% SDS-modified SPI	1.75 ± 2.36
1M GuHCl-modified SPI	39.35 ± 0.38

Table 3. Shear strength (unsoaked, soaked, and wet strength) of various SPI (82% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 2 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Shear strength		
	Unsoaked sample	Soaked sample	Wet strength
SPI	1.840 ± 0.152 MPa <i>CFF (60:100; 40:10)</i>	1.480 ± 0.066 MPa <i>CFF (100:100)</i>	0.327 ± 0.066 MPa <i>CFF (20:100; 40:70; 40:0)</i>
3% SDS-modified SPI	1.754 ± 0.121 MPa <i>CFF (100:100)</i>	1.395 ± 0.074 MPa <i>CFF (100:100)</i>	0.360 ± 0.026 MPa <i>CFF (60:100; 40:75)</i>
1M GuHCl-modified SPI	1.913 ± 0.074 MPa <i>CFF (100:100)</i>	1.869 ± 0.077 MPa <i>CFF (100:100)</i>	0.378 ± 0.012 MPa <i>CFF (40:100; 60:90)</i>

NOTE: break mode *CFF (n:m)* meant *n%* specimens showed *m%* Cohesive Failure within Fiberboard (CFF)

Table 4. Shear strength (unsoaked, soaked, and wet strength) of various SPI (90% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 2 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Shear strength		
	Unsoaked sample	Soaked sample	Wet strength
SPI	2.116 ± 0.115 MPa	1.935 ± 0.111 MPa	0.414 ± 0.030 MPa
	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>
1% SDS-modified SPI	2.008 ± 0.137 MPa	1.735 ± 0.066 MPa	0.388 ± 0.026 MPa
	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>
1M GuHCl-modified SPI	1.885 ± 0.119 MPa	1.518 ± 0.121 MPa	0.408 ± 0.009 MPa
	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>

NOTE: break mode *CFF (n:m)* meant *n%* specimens showed *m%* Cohesive Failure within Fiberboard (CFF)

Table 5. Shear strength (unsoaked, soaked, and wet strength) of the control and drying-treated 3% SDS-modified SPI (82% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 0.5 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Shear strength		
	Unsoaked sample	Soaked sample	Wet strength
Control	1.721 ± 0.127 MPa	1.640 ± 0.056 MPa	0.283 ± 0.042 MPa
	<i>CFF (40:100; 60:10)</i>	<i>CFF (40:100; 60:15)</i>	<i>CFF (30:5; 70:0)</i>
Dried at 30°C	1.624 ± 0.196 MPa	1.701 ± 0.114 MPa	0.271 ± 0.057 MPa
	<i>CFF (60:100; 40:10)</i>	<i>CFF (60:100; 40:5)</i>	<i>CFF (20:50; 80:0)</i>
Dried at 50°C	1.826 ± 0.108 MPa	1.732 ± 0.087 MPa	0.370 ± 0.021 MPa
	<i>CFF (90:100; 10:30)</i>	<i>CFF (80:100; 20:40)</i>	<i>CFF (100:100)</i>
Dried at 70°C	1.644 ± 0.085 MPa	1.458 ± 0.088 MPa	0.290 ± 0.022 MPa
	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>
Dried at 90°C	1.963 ± 0.087 MPa	1.774 ± 0.049 MPa	0.339 ± 0.021 MPa
	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>	<i>CFF (100:100)</i>

NOTE: break mode *CFF (n:m)* meant *n%* specimens showed *m%* Cohesive Failure within Fiberboard (CFF)

Table 6. Shear strength (unsoaked, soaked, and wet strength) of the control and drying-treated 3% SDS-modified SPI (82% protein content) adhesives on solid fiberboard V2S.

Condition: 100°C, 2 MPa, 5 min; Assembly time = 10 min; Stirring time = 2 hrs

	Shear strength		
	Unsoaked sample	Soaked sample	Wet strength
Control	1.754 ± 0.121 MPa <i>CFF (100:100)</i>	1.395 ± 0.074 MPa <i>CFF (100:100)</i>	0.360 ± 0.026 MPa <i>CFF (60:100; 40:75)</i>
Dried at 30°C	1.359 ± 0.153 MPa <i>CFF (100:5)</i>	1.173 ± 0.154 MPa <i>CFF (20:80; 20:10; 20:5; 40:0)</i>	0.208 ± 0.047 MPa <i>CFF (100:0)</i>
Dried at 50°C	1.802 ± 0.084 MPa <i>CFF (100:100)</i>	1.632 ± 0.146 MPa <i>CFF (100:100)</i>	0.362 ± 0.034 MPa <i>CFF (80:100; 20:50)</i>
Dried at 70°C	1.655 ± 0.087 MPa <i>CFF (100:100)</i>	1.513 ± 0.067 MPa <i>CFF (100:100)</i>	0.318 ± 0.019 MPa <i>CFF (100:100)</i>
Dried at 90°C	1.996 ± 0.043 MPa <i>CFF (100:100)</i>	1.737 ± 0.064 MPa <i>CFF (100:100)</i>	0.350 ± 0.018 MPa <i>CFF (100:100)</i>

NOTE: break mode *CFF (n:m)* meant *n*% specimens showed *m*% Cohesive Failure within Fiberboard (CFF)